10/575548
IAP15 Rec'd PCT/PTO 10 APR 2006

SPECIFICATION

HIGHLY DUCTILE CHROMIUM ALLOY CONTAINING SILVER

Technical Field

The invention of the present application relates to a novel highly ductile chromium alloy useful for rotor and stator blades of aircraft jet engines and industrial gas turbines, for a heat-resistant wheel of automobile engine turbo chargers, and for other uses, and being excellent in strength and antioxidative properties at high temperatures as well as in ductility at room temperature.

Background Art

It has been a worldwide problem to reduce the amount of release of carbon dioxide for suppressing global warming. While a counter measure for this problem in a gas turbine is to attempt to improve heat efficiency, the effort is largely restricted today by durable temperatures of rotor and stator blades. In practice, while a nickel-base heat resistant alloy is used for the rotor and stator blades today, their durable temperature is considered to be about 1100°C due to the limitation of the melting temperature.

While high temperature strength (such as creep and fatigue) is expressed by precipitation strengthening of γ' (gamma prime) -phase in the nickel-base heat resistant alloy used for the rotor and stator blade materials of the gas turbine, the durable temperature remains to be about 1100°C as described above even by a cooling and coating technique, because the melting point of this alloy is around 1350°C. Accordingly, a heat resistant alloy which can be used at higher temperatures is desired in place of conventional nickel-base heat resistant alloys (see, for example, Non-Patent Documents 1-6).

In such circumstance, since chromium-base alloys have a number of excellent properties such as high melting point, excellent corrosion resistance, anti-oxidative property and good heat conductivity with a lower density than the nickel-base alloy, they

ATTACHMENT A

are expected to be substitute alloys for the nickel-base heat-resistant alloy (see Non-Patent Document 7). However, in a current situation, the chromium-base alloy cannot overcome the problems of low ductility, low toughness and poor processability at room temperature due to a high transition temperature of ductility and brittleness, and embrittlement at room temperature caused by absorption of nitrogen. Therefore, the chromium-base alloy cannot serve as a substitute for the Ni-base alloy. While it has been made clear that addition of a certain amount of rhenium results in expression of ductility, rhenium is an expensive rare metal and the effect of addition thereof cannot be considered to be practically remarkable.

Non-Patent Document 1: Aerosp. Sci. Technol. 3 (1999) 513-523

Non-Patent Document 2: Journal of Gas Turbine Society of Japan, vol.28, No. 4 2000 14-20

Non-Patent Document 3: Journal of The Japan Institute of Metals, vol. 66, No. 9, (2002) 873-876

Non-Patent Document 4: Metallurgical and Materials Transactions A, vol.33A, Dec. 2002, 3741-3746

Non-Patent Document 5: Scripta Materialia, 49 (2003) 1041-1046

Non-Patent Document 6: Materia Japan, vol. 42, No. 9 (2003) 621-625

Non-Patent Document 7: Kogyo Zairyo (Industrial Materials), August 2003, 61-64

Accordingly, the object of the invention, out of the background as described above, is to provide a novel chromium alloy, which is able to serve practically as a substitute for the Ni-base alloy, by taking advantage of features of the chromium-base alloy such as high melting point, excellent corrosion resistance, antioxidative property and heat conductivity in addition to good ductility at room temperature.

Disclosure of Invention

A first aspect of the invention for solving the above-mentioned problems is to provide a chromium alloy comprising, as a chemical composition thereof, 0.002 to 5 atomic % of silver and the balance of chromium and inevitable impurities.

The invention also provides, in a second aspect, a chromium alloy comprising, as a chemical composition thereof, 0.1 to 5 atomic % of silver; in a third aspect, a chromium alloy comprising 0.5 to 3.5 atomic % of silver; and in a fourth aspect, a chromium alloy according to any one of the first to third aspects above further comprising 0.05 to 6.0 atomic % of silicon, 0.05 to 10 atomic % of aluminum, or 0.05 to 10 atomic % of a combined amount of silicon and aluminum.

In a fifth aspect, the invention provides a chromium alloy further comprising 10 atomic % or less of at least one of Mo, W, Re, Fe, Ru, Co, Rh, Ni, Pt and Ir as a combined amount thereof.

In a sixth aspect, the invention provides a chromium alloy produced by at least one of the methods of a single crystal solidification method, unidirectional solidification method, powder metallurgy method, forging and casting. In a seventh aspect, the invention provides a product for use at high temperatures composed mainly of any one of the chromium alloys described above.

Brief Description of Drawings

Fig. 1 is a DTA thermograph of Cr-5Ag alloy.

Fig. 2 is a graph showing the relationship between tensile plastic strain (%) and the amount of addition of Ag of the Cr-Ag alloy.

Fig. 3 is a graph showing a 0.2% yield strength as a relationship between the temperature and the amount of addition of silver.

Fig. 4 is a graph showing antioxidative property of the Cr-Ag alloy at 1100°C in air.

Fig. 5 is a graph showing antioxidative property of the Cr-Ag alloy at 1300°C in

air.

Best Mode for Carrying Out the Invention

While the invention has features as described above, the best mode for carrying out the invention will be described below.

It should be emphasized herein that a relatively low density, high melting point and good heat conductivity are maintained in the chromium alloy of the invention by adding silver to chromium to obtain a chromium-base heat resistant alloy having good ductility at room temperature. Silver as small as 0.1 atomic % should be added to chromium in order to improve tensile ductility at room temperature. The melting point rapidly decreases when the amount of addition of silver exceeds 5 atomic % with a decrease in high temperature strength. Accordingly, the amount of addition of silver is in the range of 0.002 to 5 atomic %, preferably in the range of 0.1 to 5 atomic % considering balance between ductility and strength. The amount of addition is more preferably in the range of 0.5 to 3.5 atomic %.

The chromium alloy according to the invention exhibits a single phase texture at from room temperature to a high temperature (1600°C), and the strength is expressed by solid-solution strengthening caused by addition of silver. Antioxidative property becomes remarkably excellent at a high temperature (1300°C) as compared with pure chromium.

Silicon and aluminum may be contained as described above in the silver-containing chromium alloy of the invention. Addition of silicon and aluminum is effective for further improving the antioxidative property. However, these elements are added in the range as described above since addition of too large amounts of them may decrease ductility.

While addition of Mo, W, Fe, Co and Rh may be considered for improving the strength, a too large amount of addition of these elements may decrease ductility. While addition of Ru, Pt and Ni may be also considered for improving ductility, a too large

amount of addition of these elements may increase the density and decrease the strength. While addition of Re and Ir may be also considered, a too large amount of addition of these elements is not preferable since the density is increased.

The total amount of addition of these elements should be kept at 10 atomic % or less as described above.

The invention will be described in more detail below with reference to examples. It should be noted of course that the invention is by no means restricted to these examples.

(Examples)

Example 1

Each of the chromium-silver alloys (alloys 1 to 6) with a composition shown in Table 1 was cast by arc-melting.

In Table 1, the contents of C, O, N, H, S, Si, Fe, Al, Cu and Pd in alloys 2 to 6 are shown to be the same as the contents in Alloy 1.

TABLE 1

Alloy	Composition (in atomic percent)											
	Cr	Ag	C	O	N	H	S	Si	Fe	Al	Cu	Pd
1	99.87	0	0.002	0.018	0.006	0.003	0.0002	0.006	0.09	0.003	0.0003	0.0001
2	99.77	0.1	-	-	-	-	-	-	-	-	-	-
3	99.37	0.5	-	-	-	-	-	-	-	-	-	
4	98.87	1.0	-	-	-	-	-	-	-	-	-	-
5	97.87	2.0	-	-	-	-	-	-	-	-	-	-
6	94.87	5.0	-	-	-	-	-	-	-	-	-	-

Fig. 1 shows a thermograph of a typical differential thermal analysis (DTA) in a heat cycle, wherein a chromium alloy (alloy 6) in which 5 atomic % of silver is added is heated from room temperature to 1600°C at a heating rate of 5 °C/min followed by cooling to room temperature. The results in Fig. 1 show the alloy remains a single phase in the temperature range of from room temperature to 1600°C.

Fig. 2 shows the relationship between the tensile plastic strain (%) and the amount of addition of silver (atomic %) of silver-added chromium alloys (alloys 1-6) when a plate test piece with a length of 12 mm, a width of 5 mm and a thickness of 1 mm is subjected to static drawing at room temperature.

It can be confirmed from Fig. 2 that an elongation ratio of about 24% is observed at room temperature in the chromium alloy (alloy 5) containing 2 atomic % of silver. It can be also confirmed from Fig. 2 that, with respect to the alloys containing various amounts of silver, an elongation ratio of 24% or more is observed at room temperature in the chromium alloys containing 2 to 3.4 atomic % of silver, and an elongation ratio of 13% or more is observed at room temperature in the chromium alloys containing 0.5 atomic % or more of silver. An elongation ratio of 5% is confirmed for the alloy containing 0.02 atomic % of silver. While a practical structural alloy is required to have an elongation ratio of 2% or more at room temperature, this requirements of an elongation ratio of 2% has been satisfied in the chromium alloy containing 0.002 atomic % or more of silver according to the invention.

The silver-containing chromium alloy of the invention has excellent properties with ductility of 10 to 24% at room temperature by containing a preferable amount of silver in the range of 0.5 to 3.5 atomic %. Therefore, it can be understood that the chromium alloy of the invention has sufficient and remarkable tensile ductility, considering that ductility of CMSX-4 and CMSX-10 as practical Ni-base heat resistant alloys and the Ni-base alloy TMS-75, which is developed by the inventors of the invention and has performance comparable to or superior to practical CMSX alloys, has ductility of

6 to 7% at the highest at room temperature.

Fig. 3 shows the relationship between 0.2% yield strength in the temperature range of from room temperature to 1400°C, and the amount of addition of silver. It can be known that the yield strength increases with the increase of the amount of addition of silver due to solid solution strengthening, and the yield strength shows an increase of about 50% of that of pure chromium in the alloy (alloy 6) containing 5 atomic % of silver. Although the effect of solid solution strengthening by adding silver is decreased at higher temperatures, the yield strength is higher than that of pure chromium even at 1400°C.

It is an important feature of the silver-containing chromium alloy of the invention that the yield strength (0.2% yield stress) is 50 MPa or more at 1000°C, 20 to 30 MPa or more even at 1200°C or more, and 10 MPa or more at 1400°C. While the conventional Ni-base heat resistant alloy cannot be used at a temperature of 1200°C or more, it is well possible to use the alloy according to the invention at these temperatures.

Figs. 4 and 5 show the test results of the antioxidative properties at 1100°C and 1300°C in air with respect to a silver-containing chromium alloys (alloy 3 and alloy 5) containing 0.5 atomic % of silver and 2 atomic % of silver, respectively, as compared with chromium containing no silver. As shown in Figs. 4 and 5, the alloy (alloy 5) containing 2 atomic % of silver showed an excellent antioxidative property at 1300°C in air.

Example 2

Each of the alloys with a composition shown in Table 2 was cast by arc-melting in the same manner as in Example 1.

In Table 2, the contents of C, O, N, H, S, Si, Fe, and Al in alloys 8 to 11 are shown to be the same as the contents in Alloy 7.

TABLE 2

Alloy	Composition (in atomic %)											
	Cr	Ag	Si	Ir	C	O	N	H	S	Si	Fe	Al
7	99.87	0	0	0	0.002	0.018	0.006	0.003	0.0002	0.006	0.09	0.003
8	93.87	0	6.0	0	-	-	-	-	-	-	-	-
9	91.87	2.0	6.0	0	-	-	-	-	-	-	-	
10	93.87	0	0	6.0	-	-	-	-	-	-	-	-
11	91.87	2.0	0	6.0	-	-	-	-	-	-	-	-

Of the alloys in Table 2, alloy 9 (Cr-6Si-2Ag) and alloy 11 (Cr-6Ir-2Ag) are the chromium alloys of the invention.

Table 3 shows the results of measurements of the mechanical properties (0.2% yield strength, tensile strength and elongation) at room temperature. It is confirmed in the alloys of the invention that ductility at room temperature is improved while the mechanical properties are remarkably improved.

TABLE 3

Alloy		Mechanical Properties (at room temperature)		
		0.2% Yield Strength, MPa	Ultimate Strength, MPa	Tensile Elongation, %
7	Cr	167	167	0
8	Cr-6Si	238	238	0
9	Cr-6Si-2Ag	286	332	2
10	Cr-6Ir	192	192	0
11	Cr-6Ir-2Ag	216	274	3

The chromium alloy of the invention is the first structural alloy as chromium alloy, having sufficient tensile ductility at room temperature. Since the alloy is also excellent in the strength and antioxidative strength at high temperature, it is expected to be a heat resistant part mainly for the material of a gas turbine blade. No special grade is needed with respect to the purity and production method of the material. The alloy of the invention is epoch-making as a substitute for the nickel-base heat resistant alloy.

Industrial Applicability

As hitherto described, the invention provides a novel chromium alloy, which is able to serve as a practical substitute for the conventional Ni-base alloy, by taking

advantage of features of the chromium-base alloy such as high melting point, excellent corrosion resistance, antioxidative property and heat conductivity in addition to good tenacity at room temperature.

The chromium alloy of the invention provides products for various high temperature uses such as rotor and stator blades of the aircraft jet engines and industrial gas turbines, suction and exhaust valves, rocker arms, coupling rods, and heat-resistant wheels of turbo chargers for motorcycle and automobile engines.